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| (54) Title: FUNCTIONALIZED POLYMERS | | | |
| (57) Abstract | | | |
| <p>A process for functionalizing polymers prepared by carbocationic polymerization wherein a living carbocationic polymerization system is reacted with one or more aromatic ring systems, and the use of substituted or unsubstituted reaction products of said process in lubricating oil or fuel compositions and additive concentrates, for example as dispersant, detergent or antioxidant additives or VI improvers.</p> | | | |

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FUNCTIONALIZED POLYMERS

The invention relates to a new process for functionalizing polymers prepared by carbocationic polymerization, and to new functionalized polymers, such as telechelic prepolymers.

5 Polymers having functional groups are useful as lube additives, compatibilisers, emulsifiers or as raw material for the production of adhesives, modifiers, coating material, sealing material and the like. Consequently, there has been a lively interest in
10 functionalized polymers.

 Carbocationic polymerization is one of the known routes for preparing functionalized polymers. For instance, WO-A-94/13706 discloses a method for direct synthesis by living cationic polymerization of novel
15 polymeric materials functionalized with nitrogen-containing functional groups. Polymerization and functionalization occur in a substantially simultaneous manner (e.g. in a one-step Friedel-Crafts reaction). In section II.5.2 of the textbook "Designed Polymers by
20 Carbocationic Macromolecular Engineering: Theory and Practice" (Hanser Publishers, 1991), the authors J.P. Kennedy and B. Iván provide numerous examples with additional end-groups both in polyolefins and poly(alkyl vinyl ether)s, albeit typically in a two-step process.

25 It will be understood that polymers prepared in a one-step carbocationic polymerization process having novel end-groups, with potential for further reactions, will be highly desired.

 Accordingly, a process has now been found for
30 functionalizing polymers prepared by carbocationic

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polymerization wherein a living carbocationic polymerization system is reacted with one or more aromatic ring systems.

5 The process is particularly suitable when the one or more aromatic ring systems are selected from five-, six- or seven-atom heterocycles. Such heterocycles will have one or more heteroatoms selected from N, O, P and S and typically provide the necessary electron-rich environment required for the reaction, a Friedel-Crafts
10 reaction, to occur. Preferably, the one or more aromatic ring systems are selected from six- π -electron ring systems. Examples of particularly preferred aromatic ring systems include pyrrole, furan, thiophene, oxazole, isothiazole, 1,3,4-thiadiazole, and pyrazole. These
15 aromatic ring systems may be substituted in part, provided the substituents neither sterically block the remaining reactive sites of the aromatic ring systems, nor deactivate the aromatic ring systems. For instance, the substituents may be selected from amino, hydroxy,
20 alkoxy, aminocarbonyl, alkyl or aryl groups, or halogen atoms. The first mentioned substituents are the stronger activating groups. Such substituents may be relatively large, e.g. in the case where the aromatic ring system acts as a coupling agent, the first substituent
25 corresponds (on average) to half the molecular weight of the functionalized polymer. Examples of suitable substituted aromatic ring systems include for instance 3,3-dimethyl-3H-pyrazole and 2,2-bithienyl.

30 The one or more aromatic ring systems may also be selected from (benzo-)fused ring systems, such as naphthalene, quinoline, quinoxaline, indole, the benzofurans, the benzothiophenes, pteridine, purine, indolizine and the like. Again, these one or more

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aromatic ring systems may be substituted in part with the same substituents mentioned above.

Preferably, the one or more aromatic ring systems are selected from pyrrole, furan and thiophene and substituted versions thereof. The polymers thus prepared can be further functionalized through the well known and very extensive chemistry of the pyrrole, furan and thiophene structure. An additional advantage of the use of thiophene or a substituted thiophene is the inherent anti-oxidant properties of the functionalized polymer.

Note that, as used throughout this specification, the definition of living polymers coincides with that of WO-A-94/13706 and the textbook by Kennedy and Iván mentioned above. Thus, living carbocationic polymerization systems comprise ideal living polymerizations, based on cationic initiation in which chain transfer and termination are absent and quasi living polymerizations in which rapidly reversible chain transfer and/or termination are present and the rate of these processes is faster than that of propagation. In other words, systems wherein the rate of irreversible chain transfer and/or termination is zero or appears to be zero.

As is discussed in the textbook, (living) carbocationic polymers are polymers formed by controlled initiation, i.e. by an initiator that is either monofunctional or polyfunctional, whereby the polymer chain will propagate at one end in one direction or from the centre in more directions.

Suitable living carbocationic polymerization systems are, for instance: t-alkyl esters/ BCl_3 ; cumyl acetate/ TiCl_4 ; 2,2'-bipyridyl/ TiCl_4 ; $\text{CH}_3\text{SO}_3\text{H}/\text{SnCl}_4$ + n-Bu₄NCl; HI/I_2 ; HI/ZnX_2 or SnX_2 (X = Cl, Br); HI/ZnI_2 ;

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or $\text{CH}_3\text{COClO}_4$ using as monomer(s) for instance:
isobutene; isobutene/2,4-dimethyl-1,3-pentadiene;
styrene; p-vinylphenyl glycidyl ether; isobutyl vinyl
ether; methyl vinyl ether/p-methoxystyrene; or 2-
5 methyldihydrofuran, respectively (for a more
comprehensive list see Table IV, pp. 43-55 of the
aforementioned textbook). In addition, the nitrogen-
containing compounds employed as initiator in
WO-A-94/13706 may be used, such as 2-azido-isopropyl-
10 benzene or bis(2-azido-isopropyl)benzene in admixture
with diethylaluminium chloride, TiCl_4 or BCl_3 .

Although insoluble catalysts may be used, preferably
homogeneous catalysts are used. It is common to use
solvents in the polymerization process. Suitable
15 solvents have a freezing point (well) below the
preferred polymerization temperature. Illustrative
solvents include, but are not limited to, C_2 to C_{10}
alkanes, -alkenes, -alkylhalides and -alkenylhalides,
carbon tetrachloride, carbon disulphide, nitroethane,
20 liquid carbon dioxide and methylcyclohexane. Mixed
solvents can also be used. The preferred solvents are
the low-boiling alkylhalides: chloroform, methylene
dichloride, methyl chloride, ethyl chloride, propyl
chloride, n-butyl chloride, and 1,2-dichloroethane; and
25 neopentane, hexane, heptane and purified petroleum
ether.

Any cationically polymerizable monomer may be used,
including straight and branched chain alpha-olefins,
isoolefins, alicyclic monoolefins, cycloaliphatic
30 compounds, styrene derivatives, indene and derivatives,
and other monoolefins and heterocyclic cationically
polymerizable monomers identified in the text by
Kennedy, "Cationic Polymerization of Olefins: A Critical

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Inventory"; pp. 39-53 (Wiley, 1975). Vinyl ethers can also be used.

Particularly valuable polymers can be prepared from isoolefins of from 4 to 20 carbon atoms or mixtures thereof. Examples of such unsaturated hydrocarbons include, but are not restricted to, isobutene, 2-methylbutene, 3-methyl-1-butene, 4-methyl-1-pentene, and beta-pinene. Other cationically polymerizable monomers that may be employed include heterocyclic monomers such as oxazolines and others known to add on to polarized covalent bonds. Mixtures of cationically polymerizable monomers can be employed as feedstock to the polymerization zone if desired. Thus, copolymers, terpolymers and higher interpolymers can be prepared by employing a mixture of two, three or more of the above monomers. Preferred feedstocks to the polymerization zone comprise pure isobutene and mixed C₄ hydrocarbon feedstocks containing isobutene, such as a C₄ cut resulting from the thermal or catalytic cracking operation of, for example, naphtha. Suitable isobutene feedstocks will typically contain at least 10%, and up to 100% isobutene by weight on the weight of the feed. Conventional C₄ cuts suitable for use as a feedstock, which are of industrial importance, typically will contain between 10 and 40% 1-butene, between 10 and 40% 2-butene, between 40 and 60% isobutane, between 4 and 10% n-butane, and up to about 0.5% butadiene, all percentages being by weight based on the feed weight. Feedstocks containing isobutene may also contain other non-C₄ polymerizable olefin monomers in minor amounts, e.g. typically less than 25%, preferably less than 10%, and most preferably less than 5%, such as propadiene, propylene and C₅ olefins. The term "polyisobutene" as

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employed herein is intended to include not only homopolymers of isobutene but also copolymers of isobutene and one or more other C₄ polymerizable monomers of conventional C₄ cuts as well as non-C₄ ethylenically unsaturated olefin monomers containing typically from 3 to 6, and preferably from 3 to 5 carbon atoms, provided such copolymers contain typically at least 50%, preferably at least 65%, and most preferably at least 80% isobutene units, by weight, based on the polymer number average molecular weight (M_n). The substantially selective polymerizability of isobutene under the conditions specified herein ensures that minimum isobutene content described above.

Preferably the polymerization medium is substantially free of poisons to the catalyst. For instance, the olefin feed can be treated by use of molecular sieves and subjected to caustic washing to remove, e.g. mercaptans, water, and dienes (if desired).

The polymerization reaction may be conducted batchwise, or in a (semi)continuous operation in which continuous streams of ingredients are delivered to the reactor and an overflow of a slurry or solution of polymer is taken out for the recovery of the polymer therefrom. From an operational point of view, the preferred mode of reaction is on a continuous basis using a continuous flow stirred reactor wherein, in a controlled manner, feed is continuously introduced into the reactor and product is continuously removed from the reactor. However, in case a more well defined (narrow molecular weight distribution) product is to be produced, a batch process is preferred.

The amount of catalyst employed in the process of the present invention can be varied to achieve the

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target number average molecular weight of polymer. Varying the amounts may also minimize or reduce undesired isomerizations. The lower the initiator concentration in the reaction phase, the higher will be the polymer molecular weight and vice versa. Control of the polymer molecular weight within defined limits of a selected target polymer molecular weight is particularly important when the polymer is intended for use in lubricating oils as a dispersant. The catalyst amount also affects the conversion of the olefin monomer and yield of polymer, with higher amounts of catalyst typically achieving higher conversion and yields. The catalyst should be employed in sufficient amount to enable the reaction to be a "living" cationic polymerization.

The polymerization reaction is conducted in the liquid phase to induce linear or chain type polymerization instead of ring or branch formation. If a feed is used which is gaseous under ambient conditions, it is preferred to control the reaction pressure and/or dissolve the feed in an inert solvent or liquid diluent, in order to maintain the feed in the liquid phase. Typical C₄ cuts used as feed are liquid under pressure and do not need a solvent or diluent. If under normal circumstances the selected catalyst is a gas (e.g. BF₃ and the like) the gaseous catalyst is typically partially or completely dissolved in a pressurized liquid after introduction in the reactor. Polymerization pressures can range typically from 25 to 500, and preferably from 100 to 300 kPa.

The temperature at which the polymerizations are carried out is important, since temperatures that are too high tend to decrease the functionalization degree.

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The usual polymerization temperature range is between -100 °C and +10 °C. Preferably, the polymerizations are performed at a temperature below -10 °C, preferably below -20 °C, and preferably between -80 °C and -20 °C, e.g. at a temperature of -50 °C. The liquid phase reaction mixture temperature is controlled by conventional means. The particular reaction temperature is selected to achieve the target living polymerization behaviour, and preferably is not allowed to vary more than + or - 5 °C from the selected value, while the catalyst and/or promoter feed rate is varied to achieve the desired Mn to compensate for variations in monomer distribution in the feed composition.

Average polymerization times, in minutes, can vary from 10 to 120, preferably from 15 to 45, more preferably 15 to 30, and most preferably from 15 to 25.

The reaction, which is a Friedel-Crafts alkylation reaction, will occur under the same conditions required to form the carbocationic polymerization system. These conditions will therefore be readily familiar to the persons skilled in this art. Besides, Friedel-Crafts alkylation reactions are well-known and examples of suitable conditions and references to further examples may, for instance, be found in "Advanced Organic Chemistry" by J. March (section 1-13 of 3rd edition; Wiley, 1985). Typical conditions involve some form of temperature control to remove the heat of reaction, a solvent and a means to bring the reagents into contact (stirrer, etc.).

The materials used to quench the reaction are conventional and include the same materials commonly used as cationic polymerization promoters (e.g. moisture, alcohol) with the exception that excess

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quantities are employed in amounts sufficient to deactivate the catalyst. Thus, while any amount of quenching medium effective to deactivate the catalyst may be employed, it is contemplated that such effective amount be sufficient to achieve a molar ratio of quench medium to catalyst of typically from 1:1 to 100:1, preferably from 3:1 to 50:1, and most preferably from 10:1 to 30:1. Quench is conducted by introducing the quench medium into the polymer product. Typically, the polymer product is maintained under pressure during the quench sufficient to avoid vaporisation of any gaseous catalyst (if one is employed) and other components of the mixture. The temperature of the quenching medium is not critical and e.g. can comprise room temperature or lower. In a batch system, quench can be performed in the reactor or preferably on the product after it is withdrawn from the reactor. In a continuous system, the quench will typically be performed after product exits the reactor. After quench, the polymerization product is typically subjected to conventional finishing steps that include a caustic/H₂O wash to extract catalyst residue, a hydrocarbon/aqueous phase separation step wherein deactivated and extracted catalyst is isolated in the aqueous phase, and a water washing step to remove residual amounts of neutralized catalyst. The polymer is then typically stripped in a debutanizer to remove unreacted volatile monomers, followed by a further stripping procedure to remove light end polymer (e.g. C₂₄ carbon polymer). The stripped polymer is then typically dried by N₂.

In principle, the one or more aromatic ring systems may be introduced during the preparation of the carbocationic polymerization system, although a better

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defined product is prepared when the living carbocationic polymerization systems have exhausted the supply of monomers. Depending on the ratio of living carbocationic polymerization systems per amount of one or more aromatic ring systems, and depending on the functionality of the initiating system, polymers may be prepared having the functional end-group at one terminus of the polymer chain (1:1; monofunctional), having the one or more aromatic ring systems coupling two or more living carbocationic polymerization systems (so-called branched or star-branched polymers prepared e.g. in a ratio of 2 or more:1; monofunctional), having living carbocationic polymerization systems end-capped at some or each of the propagating termini (so-called telechelic prepolymers prepared e.g. in a ratio of 2:1; bifunctional or 3:1; trifunctional, etc.), and even mixed systems where the one or more aromatic ring systems act as both coupling agent and as functional end-group when a polyfunctional initiator is used.

Examples include, but are not limited to:

I-P-Ar

I-P-Ar-(P-I)_n

Ar-P-I'-(P-Ar)_m

Ar-P-I''-P-Ar-P-I''-P-Ar

wherein Ar represents the one or more aromatic ring systems, P represents the polymer (e.g. homopolymer, random or block copolymer, etc.), I represents the monofunctional initiator, I' represents the polyfunctional initiator, I'' represents the bifunctional initiator, and n and m are numerals corresponding to the functionality of the one or more aromatic ring systems, or the polyfunctional initiator, respectively.

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Preferred are telechelic prepolymers that are capped by one or more functional terminal groups and branched or star-branched polymers that are coupled by one or more polyfunctional coupling groups, wherein said terminal groups and said polyfunctional coupling groups are five-atom, six- π -electron heterocycles. Said branched or star-branched polymers are preferably capped by one or more functional terminal groups, wherein said terminal groups are five-atom, six- π -electron heterocycles.

The telechelic prepolymers and the branched or star-branched polymers, particularly those capped by more than one functional terminal group, are useful in the preparation of high molecular weight products, including networks and VI (viscosity index) improvers.

The substituted or unsubstituted reaction product of the present invention may, as well as a VI improver, be used, for example, as a dispersant or antioxidant additive in lubricating oils. Accordingly, the present invention provides a lubricating oil composition comprising a major amount (more than 50%w) of a lubricating base oil and a minor amount (less than 50%w), preferably from 0.1 to 20%w, especially from 0.5 to 10%w (active matter), of a substituted or unsubstituted reaction product according to the present invention, the percentages by weight being based on the total weight of the composition.

A lubricant formulation may be produced by addition of an additive package to the lubricating oil. A minor amount of viscosity modifier may be included if the final lubricant formulation is to be a multigrade version. The type and amount of additive package used in the formulation depends on the final application,

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which can include spark-ignition and compression-ignition internal combustion engines, including automobile and truck engines, marine and railroad diesel engines, gas engines, stationary power engines and turbines.

The lubricant formulation is blended to meet a series of performance specifications as classified in the US by a tripartite arrangement between the Society of Automotive Engineers (SAE), American Petroleum Institute (API) and American Society for Testing and Materials (ASTM). Also the American Automobile Manufacturers Association (AAMA) and Japan Automobile Manufacturers Association Inc. (JAMA), via an organisation called the International Lubricant Standardisation and Approval Committee (ILSAC), jointly develop minimum performance standards for gasoline-fuelled passenger car engine oils.

In Europe, engine oil classifications are set by the Association des Constructeurs Europeens de l'Automobile (ACEA) in consultation with the Technical Committee of Petroleum Additive Manufacturers (ATC) and Association Technique de l'Industries Europeens des Lubrifiants (ATIEL). Besides these internationally recognised oil classification systems, many, if not all, Original Equipment Manufacturers (OEMs) have their own in-house performance requirements that must be met by lubricant formulations used for first (i.e. factory) fill.

Suitable lubricating base oils are natural, mineral or synthetic lubricating oils.

Natural lubricating oils include animal and vegetable oils, such as castor oil. Mineral oils comprise the lubricating oil fractions derived from crude oils, e.g. of the naphthenic or paraffinic types

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or mixtures thereof, coal or shale, which fractions may have been subjected to certain treatments such as clay-acid, solvent or hydrogenation treatments. Synthetic lubricating oils include synthetic polymers of

5 hydrocarbons, e.g. derived from polyalphaolefins, isomerised slack wax, modified alkylene oxide polymers and esters, which are known in the art. These lubricating oils are preferably crankcase lubricating oil formulations for spark-ignition and compression-

10 ignition engines, but include also hydraulic lubricants, metal-working fluids and automatic transmission fluids.

Preferably the lubricating base oil component of the compositions according to the present invention is a mineral lubricating oil or a mixture of mineral

15 lubricating oils, such as those sold by member companies of the Royal Dutch/Shell Group of Companies under the designations "HVI", or the synthetic hydrocarbon base oils sold by member companies of the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trade

20 mark).

The viscosity of the lubricating base oils present in the compositions according to the present invention may vary within wide ranges, and is generally from 3 to 35 mm²/s at 100°C.

25 The lubricating oil compositions according to the present invention may contain various other additives known in the art, such as:

(a) Viscosity index improvers or modifiers. The viscosity modifier may be of the solid type or a

30 concentrate in a natural or synthetic base stock and can be defined as a substance, usually a polymer, which substantially improves (e.g. by at least 5 units) the viscosity index (e.g. as determined by

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ASTM procedure D2270) by its incorporation. These can all be incorporated into the final lubricant formulation to give the desired performance properties thereof. Examples of such viscosity modifiers are linear or star-shaped polymers of a diene such as isoprene or butadiene, or a copolymer of such a diene with optionally substituted styrene. These copolymers are suitably block copolymers and are preferably hydrogenated to such an extent as to saturate most of the olefinic unsaturation. A number of other types of viscosity modifier are known in the art, and many of these are described in Proceedings of Conference "Viscosity and flow properties of multigrade engine oils", Esslingen, Germany, December 1977. It is also known in the art that viscosity modifiers can be functionalised to incorporate dispersancy (e.g. dispersant viscosity index improvers based on block copolymers, or polymethacrylates) and/or antioxidant functionality as well as viscosity modification and they can also have pour point depressants mixed in to give handleable products in cold climates.

- (b) Ashless or ash-containing extreme pressure/anti-wear additives, such as, for example, those of the metal containing dithiophosphate or ashless dithiocarbamate type, and mixtures thereof. The actual composition of the individual components will vary depending upon final application and hence can be based on a range of metal ion types and various alcohols, in which both alkyl and aryl moieties may be of varying size. Preferred are zinc dithiophosphates (ZDTPs) or sodium dithiophosphates.

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- (c) Dispersants including succinimides and Mannich bases, both of various molecular weights and amine type, including borated versions, or esters also of varying type and molecular weight. Preferred are ashless dispersants such as polyolefin-substituted succinimides, e.g. those described in GB-A-2231873.
- (d) Anti-oxidants, for example of the aminic type such as "IRGANOX" (trade mark) L57 (tertiary C₄-C₁₂ alkyl diphenylamine) or phenolic type such as "IRGANOX" (trade mark) L135 (2,6-ditertiary-butyl-4-(2-carboxy(alkyl)ethyl)phenol) (ex. CIBA Speciality Chemicals) or a soluble copper compound at a copper concentration of between 50 and 500 ppm.
- (e) Anti-rust compounds of, for example, the ethylene/propylene block copolymer type.
- (f) Friction modifiers for fuel economy, either metal (e.g. molybdenum) containing, or metal free esters and amines, or synergistic mixtures thereof.
- (g) Metal containing detergents such as phenates, sulphonates, salicylates or naphthenates, or mixtures thereof, all of which detergents may be either neutral or overbased, such overbased detergents being carbonates, hydroxides or mixtures thereof. The metals are preferably calcium, magnesium or manganese, although alkali metals such as sodium or potassium could also be used.
- (h) Copper passivators, preferably of the alkylated or benzylated triazole type.

The reaction product of the present invention may also be used as an additive in fuels, for example as a dispersant or detergent additive. Accordingly, the present invention further provides a fuel composition comprising a major amount (more than 50%w) of a base

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fuel and a minor amount (less than 50%w), preferably from 0.001 to 2%w, more preferably from 0.001 to 0.5%w and especially from 0.002 to 0.2%w (active matter), of a reaction product according to the present invention, the percentages by weight being based on the total weight of the composition.

Suitable base fuels include gasoline and diesel fuel. These base fuels may comprise mixtures of saturated, olefinic and aromatic hydrocarbons, and may contain a range of sulphur levels, e.g. in the range 0.001 to 0.1%w. They can be derived from straight-run gasoline, synthetically produced aromatic hydrocarbon mixtures, thermally catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions or catalytically reformed hydrocarbons.

The fuel compositions according to the present invention may contain various other additives known in the art, such as:

- (a) Anti-knock additives, such as lead compounds, or other compounds such as methyl cyclopentadienyl-manganese tricarbonyl or orthoazidophenyl.
- (b) Co-antiknock additives, such as benzoylacetone.
- (c) Dehazers, such as those commercially available as "NALCO" (trade mark) EC5462A (ex. Nalco), "TOLAD" (trade mark) 2683 (ex. Baker Petrolite), EXP177, EXP159M, EXP175, EP409 or EP435 (ex. RE Speciality Chemicals), and T9360-K, T9305, T9308, T9311 or T327 (ex. Baker Petrolite).
- (d) Anti-foaming agents, such as those commercially available as "TEGOPREN" (trade mark) 5851, Q 25907, MR1027, MR2068 or MR2057 (ex. Dow Corning), "RHODORSIL" (trade mark) (ex. Rhone Poulenc), and

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"WITCO" (trade mark) SAG TP325 or SAG327 (ex. Witco).

- 5 (e) Ignition improvers (e.g. 2-ethylhexyl nitrate, cyclohexyl nitrate, di-tertiary-butyl peroxide and those disclosed in US-A-4208190 at Column 2, line 27 to Column 3, line 21)
- 10 (f) Anti-rust agents (e.g. that commercially sold by Rhein Chemie, Mannheim, Germany as "RC 4801", or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms (e.g. the pentaerythritol diester of polyisobutylene-
- 15 substituted succinic acid))
- (g) Reodorants.
- (h) Anti-wear additives.
- 20 (i) Anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine).
- (j) Metal deactivators.
- (k) Lubricity agents, such as those commercially available as EC831, "PARADYNE" (trade mark) 631 or 655 (ex. Paramins) or "VEKTRON" (trade mark) 6010
- 25 (ex. Shell Additives International Limited).
- (l) Carrier fluids such as a polyether e.g. a C₁₂-C₁₅ alkyl-substituted propylene glycol ("SAP 949"), "HVI" or "XHVI" (trade mark) base oil, which are commercially available from member companies of the
- 30 Royal Dutch/Shell Group of Companies, a polyolefin derived from C₂-C₆ monomers, e.g. polyisobutylene having from 20 to 175, particularly 35 to 150, carbon atoms, or a polyalphaolefin having a

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viscosity at 100°C in the range 2×10^{-6} to 2×10^{-5} m²/s (2 to 20 centistokes), being a hydrogenated oligomer containing 18 to 80 carbon atoms derived from at least one alphaolefinic monomer containing from 8 to 18 carbon atoms.

The lubricating oil and fuel compositions of the present invention may be prepared by adding the substituted or unsubstituted reaction product of the present invention to a lubricating base oil or base fuel. Conveniently, an additive concentrate is blended with the lubricating base oil or base fuel. Such a concentrate generally comprises an inert carrier fluid and one or more additives in a concentrated form. Hence the present invention also provides an additive concentrate comprising an inert carrier fluid and from 10 to 80%w (active matter) of a substituted or unsubstituted reaction product according to the present invention, the percentages by weight being based on the total weight of the concentrate.

Examples of inert carrier fluids include hydrocarbons and mixtures of hydrocarbons with alcohols or ethers, such as methanol, ethanol, propanol, 2-butoxyethanol or methyl tert-butyl ether. For example, the carrier fluid may be an aromatic hydrocarbon solvent such as toluene, xylene, mixtures thereof or mixtures of toluene or xylene with an alcohol. Alternatively, the carrier fluid may be a mineral base oil or mixture of mineral base oils, such as those sold by member companies of the Royal Dutch/Shell Group of Companies under the designations "HVI", e.g. "HVI 60" base oil, or the synthetic hydrocarbon base oils sold by member companies of the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trade mark).

Non-limiting examples of suitable additive concentrations in final blended lubricating oil compositions are:

| Oil component & mass | A | B | C | D | E | F |
|-------------------------------------|---------|---------|---------|---------|---------|---------|
| Alkaline earth sulphonate detergent | 3.8 | 3.4 | - | - | - | - |
| Alkaline earth phenate detergent | 1.2 | 1.1 | - | - | - | - |
| Alkaline earth salicylate detergent | - | - | 4.6 | 2.5 | 3.6 | 10.5 |
| High molecular weight dispersant | - | 5.5 | 8.0 | 5.0 | 11.5 | - |
| Low molecular weight dispersant | 6.0 | 2.0 | - | - | - | 9.0 |
| Primary ZDTP | 0.5 | - | - | 0.3 | - | 0.7 |
| Secondary ZDTP | 0.4 | 1.0 | 0.9 | 0.7 | 1.2 | 0.6 |
| Aminic antioxidant | - | - | 0.6 | 0.8 | 0.3 | - |
| Phenolic antioxidant | 0.7 | 1.2 | - | - | - | - |
| Base oil | balance | balance | balance | balance | balance | balance |

Non-limiting examples of suitable additive concentrates for blending lubricating oil compositions are:

| Oil component & mass | A | B | C | D | E | F |
|--------------------------------------|---------|---------|---------|---------|---------|---------|
| Alkaline earth sulphonate detergent | 29.9 | 23.8 | - | - | - | - |
| Alkaline earth phenate detergent | 9.4 | 7.7 | - | - | - | - |
| Alkaline earth salicyclate detergent | - | - | 32.4 | 26.6 | 21.6 | 50.2 |
| High molecular weight dispersant | - | 38.5 | 56.3 | 53.2 | 68.9 | - |
| Low molecular weight dispersant | 47.2 | 14.0 | - | - | - | 43.1 |
| Primary ZDTP | 3.9 | - | - | 3.2 | - | 3.3 |
| Secondary ZDTP | 3.1 | 7.0 | 6.3 | 7.4 | 7.2 | 2.9 |
| Aminic antioxidant | - | - | 4.2 | 8.5 | 1.8 | - |
| Phenolic antioxidant | 5.5 | 8.4 | - | - | - | - |
| Base oil | balance | balance | balance | balance | balance | balance |

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The present invention still further provides the use of a substituted or unsubstituted reaction product according to the present invention as a dispersant, detergent or antioxidant additive or VI improver.

5 The following examples illustrate the invention. Examples 1 to 5 are model experiments. They use a living carbocationic dimerisation system derived from 2-chloro-2,4,4-trimethylpentane, thus resembling the dimer of isobutene, instead of a living carbocationic polymerization system as reagent. Examples 6 to 10
10 illustrate products of the invention using polyisobutene as polymeric component. Finally, example 11 concerns an antioxidant test of a thiophene-functionalized PIB, illustrative of an application for the novel products of
15 the invention, whereas example 12 illustrates the dispersancy properties of functionalized PIBs.

Typically, the examples were conducted in a batch reactor dipped in an external cold bath. Solvents and reagents were all thoroughly dried. In the examples the
20 following abbreviations are used:

| | |
|---------|---|
| CTMP | 2-chloro-2,4,4-trimethylpentane |
| tmb | 1,1,3,3-tetramethylbutyl (radical) |
| PIB | polyisobutene or its radical |
| IB | isobutene |
| 25 MCH | methylcyclohexane |
| DCM | dichloromethane |
| MeOH | methanol |
| TH | Thiophene |
| BrTH | 2-bromothiophene |
| 30 MeTH | 2-methylthiophene |
| BTH | 2,2'-bithienyl |
| DBTH | 3-dodecyl-2,2-bithienyl |
| DTHCE | 1,1-di(2-thienyl)-2,2,2-trichloroethane |

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FU furane
Me-FU 2-methylfurane
DtBP 2,6-di-tert.-butylpyridine.

Synthesis DBTH

5 DBTH is prepared by reaction of 3-bromoBTH with dodecyl magnesium bromide. 3-BromoBTH is prepared by reacting 2-thiophene magnesium bromide with BrTH in the presence of 1,1'-bis(diphenylphosphino)ferrocene.

Example 1

10 In a three necked round bottom 250 ml flask, equipped with a magnetic stirrer, 305 mg (2.05 mmol) CTMP is introduced, followed by 40 ml of 60:40 v/v MCH/DCM and 1385 mg (10.02 mmol) of cis-decaline (internal standard). The reactor is then cooled down to
15 -80 °C, whereupon 1869 mg (9.85 mmol) TiCl₄ dissolved in 40 ml MCH/DCM is added. Next 90 mg (1.07 mmol) TH dissolved in 20 ml MCH/DCM is added. At intervals, 2 ml samples are taken, that are quenched with 2 ml MeOH at -80 °C and analysed by gas liquid chromatography.

20 GLC revealed the conversion grade and the ratio between the end-capped and coupled products, 2-(tmb)TH (I) and 2,5-bis(tmb)TH (II). After a period of 2 hours, the conversion grade reached 60 % (on intake TH) and a product ratio I/II of 83/17. After a night
25 stirring, allowing for the mixture to warm up to room temperature, a conversion of 97.4 percent was reached at a ratio of 54/36.

Example 2

30 Under conditions similar to Example 1, no reaction took place when TH was replaced with 1.28 g (10 mmol) 2-acetylTH. Obviously, the 2-acetyl group is a deactivating group.

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Example 3

Under conditions similar to Example 1, 1.32 g 2-methyl-5(tmb)FU is produced (conversion of 68%) in half an hour when the TH is replaced by 0.82 g (10 mmol) of Me-FU. The following analytical data were found:
¹H-NMR (300 MHz, CDCl₃): 0.76 (s, 9H), 1.29 (s, 6H), 1.63 (s, 2H), 2.26 (d, 3H), 5.82 (m, 2H);
¹³C-NMR (75 MHz, CDCl₃): 14.0, 30.1, 31.2, 32.0, 5.9, 54.8, 104.0, 106.0, 150.1, 161.4 ppm.

Example 4

In a three necked round bottom 250 ml flask, equipped with a magnetic stirrer, 7.55 g (51 mmol) CTMP is introduced followed by 5.0 g (51 mmol) MeTH dissolved in 20 ml of DCM. Slowly 0.870 g (6.13 mmol) BF₃.OEt₂ is added and the reaction is followed by GLC. According to the GLC data, the monoalkylation product was immediately formed after addition of the Lewis acid, with some minor dialkylation product being formed.

The crude product is washed, dried and subjected to partial distillation (kugelrohr). A conversion of 19 percent of MeTH into 2-methyl-5(tmb)TH was found.

Example 5

The procedure of Example 1 is followed, using 0.555 g (3.75 mmol) CTMP dissolved in 10 ml 40:60 v/v hexane:DCM; 3.55 g (18.75 mmol) TiCl₄ dissolved in 20 ml of said solvent; and 0.60 g (1.875 mmol) of DBTH dissolved in 20 ml of said solvent. The progress of the reaction is determined by GC wherein two separate peaks of equal size are identified, shown (by GC-MS) to be related to 5-(tmb)DBTH and 5'-(tmb)DBTH. A conversion of 75 % was achieved.

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Example 6

PIB-functionalization experiments have been carried out with TH, BrTH, MeTH, DTHCE, DBTH, FU, and MeFU.

5 The isobutene polymerizations were carried out by a simple laboratory polymerization process in a CH₂Cl₂/hexane solvent mixture at -78 °C. The aromatic ring systems were added after reaching high (~ 100%) monomer conversion. The changes in the structure of the chain ends were investigated by UV spectroscopic
10 detector during GPC runs and by ¹H NMR spectroscopy.

The experimental conditions for the end-capping with BrTH is as follows: The reactor is filled with 6.2 mmol CTMP, 5.2 mmol 2,2'-bipyridyl, 150 ml CH₂Cl₂ and 350 ml hexane. This solution is cooled to -78 °C, whereupon
15 5 ml IB is added followed by 100 ml TiCl₄ dissolved in CH₂Cl₂ (0.18 M). 5 and 10 minutes later a further 4 ml IB were added. When the polymerization was completed, 31 mmol BrTH dissolved in 100 ml (prechilled) CH₂Cl₂ was added thereto and the reaction was monitored over time
20 (using prechilled methanol as quenching agent).

The experimental conditions for the end-capping with MeTH is as follows: The reactor is filled with 3.6 mmol CTMP, 2.4 mmol 2,2'-bipyridyl, 50 ml CH₂Cl₂ and 140 ml hexane. This solution is cooled to -78 °C, whereupon
25 5 ml IB is added followed by 50 ml TiCl₄ dissolved in CH₂Cl₂ (0.24 M). 5 and 10 minutes later a further 5 ml IB were added. When the polymerization was completed, 10 mmol MeTH dissolved in 50 ml (prechilled) CH₂Cl₂ was added thereto and the reaction was monitored over time
30 (using prechilled methanol as quenching agent).

Both BrTH and MeTH resulted in quantitative conversion of the chain ends of polyisobutene (PIB) to the corresponding heterocyclic functionalities. The

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reaction between the carbocationic chain ends and these compounds are relatively fast processes; UV analysis indicated quantitative conversion in 30 to 45 minutes with BrTH, respectively 10 to 20 minutes with MeTH.

5 ¹H NMR spectra show signals at 6.55 (d, 2H), 6.80 (d, 2H) for 2-bromo-thiophene and 6.50 (d, 2H), 6.55 (d, 2H) for 2-methyl-thiophene, which illustrates the formation of the corresponding chain ends upon functionalization with BrTH and MeTH, respectively. It is noteworthy that aromatic signals appear for the heterocyclic chain ends, and there is no signal at 1.94 ppm for the -CH₂- group characteristic for the tertiary chlorine chain end in PIBs quenched with nucleophiles not reacting with the cationic chain ends. 10 The spectroscopic results (UV and NMR) indicate quantitative end-quenching with BrTH and MeTH. 15

Coupling of living PIB chains was also attempted by bisthienyls. UV signals in GPC indicate efficient addition of the bisthienyls to the chain ends. However, 20 molecular weight data confirm neither DBTH nor DTHCE led to coupling of the chains. Warming up the polymerization system to room temperature in the presence of DBTH did not lead to coupling either.

It was also found by preliminary experiments that 25 furan and 2-methylfuran also react with the living PIB chains.

Example 7

The isobutene polymerization was carried out at -78 °C using 33 mmol CTMP, 49 mmol DtBP and 131 mmol 30 TiCl₄ as initiating system; 600 ml of 60:40 v/v MCH/DCM as solvent and 1114 mmol IB. After 1 hour 31 mmol MeTH was added. A quantitative conversion was found into 2-methyl-5(PIB)TH in 30 minutes.

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Example 8

The isobutene polymerization was carried out at -78 °C using 16.5 mmol CTMP, 4.2 mmol DtBP and 63 mmol TiCl₄ as initiating system; 600 ml of 60:40 v/v MCH/DCM as solvent and 604 mmol IB. The polymer formed had a number average molecular weight of 2244. After 1 hour 7.3 mmol TH was added. A quantitative conversion was found in 30 minutes. The product was determined to comprise both 2-(PIB)TH (Mn of 2575) and 2-5-di(PIB)TH (Mn of 3121).

Example 9

The isobutene polymerization was carried out at -78 °C using 16.8 mmol CTMP, 24 mmol DtBP and 65 mmol TiCl₄ as initiating system; 600 ml of 60:40 v/v MCH/DCM as solvent and 566 mmol IB. After 0.5 hour 21 mmol MeFU was added. A quantitative conversion was found into 2-methyl-5(PIB)FU in 30 minutes.

Example 10

The isobutene polymerization was carried out at -78 °C using 60 mmol CTMP, 30.1 mmol 2,2'-dipyridyl and 562.5 mmol TiCl₄ as initiating system; 1200 ml of 60:40 v/v MCH/DCM as solvent and 916 mmol IB. After 1 hour 50% of the solution is removed. To the remaining solution 60 mmol ethyl-2-thiopheneacetate was added. After 2 hours GPC, ¹H and ¹³C-NMR confirmed the presence of the desired functionalized PIB.

Example 11

A fully formulated oil (comprising dispersant, detergent, zinc dithiophosphate as extreme pressure anti-wear agent, and 1 %wt of 2-methylthienyl capped PIB of Mn of 1500 and 3500 respectively) was subjected to an antioxidancy test using Isothermal Differential Scanning Calorimetry (DSC) analysis.

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The analysis was carried out using two Mettler-Toledo instruments (DSC27HP). Thus, a 2.00 ± 0.05 mg of sample was placed in an aluminium pan and loaded into the DSC apparatus. Oxygen pressure and flow rate were then set to 3.4 MPa (500 psig) and 60 normal ml/min respectively using Brooks pressure and mass flow controllers. The sample was rapidly heated to the test temperature of 200 °C by overriding the ramp rate control. Power output was then monitored while holding the sample at the test temperature. The induction period was measured by taking the intercept of the tangent to the point of maximum slope on the rising side of the exothermic peak, identified by taking the derivative of the enthalpogram, with the baseline.

The test revealed the samples to have mean induction periods of 13.7 and 13.6 minutes respectively, as compared to a mean induction period of 10.9 minutes for the formulated oil without the 2-methylthienyl capped PIB.

In other words, these 2-methylthienyl capped PIBs are effective antioxidants.

Example 12

The product of example 10 ($M_n = 3180$; 3.0 mmol) and N,N-dimethyl-1,3-diaminopropane (DAP; 150 mmol) were placed in a three neck flask with reflux condenser and heated for 10 hours at 130 °C. The excess of DAP was removed under vacuum. The reaction mixture was diluted with hexane (60 ml) and washed with methanol (3x 30 ml). The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed leaving a highly viscous material. Yield: 75%.

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^{13}C -NMR: clear sign of bonded thienyl and bonded DAP carbons at 170.1, 157.7, 133.4, 126.5 and 122.2 ppm, and 58.8, 58.4 and 45.3 ppm, respectively.

5 IR: clear sign of amide carbonyl at 1660 cm^{-1} and no ester carbonyl.

Element analysis: 1.07 %w N, 0.90 %w S.

The product of Example 12 was subjected to a dispersancy test using a Bohlin VOR (Viscometry-Oscillation-Relaxation) rheometer in its viscometry
10 mode. The sample (25g) was blended into a HVI-65 NS base oil using a hotplate and magnetic stirrer bar, at a temperature of 60 to 85 °C. The active matter level was 2% w. 1.25g of carbon black (Cabot Vulcan XC72R) was
15 weighed into a 150 ml Schott bottle and the hot blended oil complete with stirrer bar was poured on to the carbon black and allowed to drain. A lid was put on the bottle and it was transferred to a heated stirrer block set to 100 °C, where it was allowed to equilibrate with
20 heat and stirring. The hot sample was then poured into the hot cup of the rheometer geometry, where it was determined by comparison with a reference sample that it reduced the viscosity of the carbon black-containing formulation by 66% at a shear rate of 0.2 s^{-1} .

25 In other words, these functionalized PIBs are effective dispersants.

C L A I M S

1. A process for functionalizing polymers prepared by carbocationic polymerization wherein a living carbocationic polymerization system is reacted with one or more aromatic ring systems.
- 5 2. A process as claimed in claim 1, wherein the one or more aromatic ring systems are selected from five-, six- or seven-atom heterocycles.
3. A process as claimed in claim 2, wherein the one or more aromatic ring systems are heterocycles comprising
10 one or more heteroatoms selected from nitrogen, oxygen, phosphor and sulphur.
4. A process as claimed in claim 1 or 2, wherein the one or more aromatic ring systems are selected from six- π -electron ring systems.
- 15 5. A process as claimed in any one of the preceding claims, wherein the one or more aromatic ring systems are selected from the heterocycles pyrrole, furan, thiophene, oxazole, isothiazole, 1,3,4-thiadiazole, pyrazole, from the substituted versions of these
20 heterocycles, and from substituted and unsubstituted (benzo-)fused ring systems, provided the substituents, if any, neither sterically block the remaining reactive sites of the aromatic ring systems, nor deactivate the aromatic ring systems.
- 25 6. A process as claimed in any one of the preceding claims, wherein the one or more aromatic ring systems are selected from heterocycles pyrrole, furan, thiophene, and from the substituted versions of these heterocycles, provided the substituents, if any, neither

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sterically block the remaining reactive sites of the aromatic ring systems, nor deactivate the aromatic ring systems.

5 7. A process as claimed in claim 5 or 6, wherein the substituents are amino, hydroxy, alkoxy, aminocarbonyl, aryl or alkyl groups, or halogen atoms.

8. Telechelic prepolymers that are capped by one or more functional terminal groups, wherein the terminal groups are five-atom, six- π -electron heterocycles.

10 9. Branched or star-branched polymers that are coupled by one or more polyfunctional coupling groups, wherein the polyfunctional coupling groups are five-atom, six- π -electron heterocycles.

15 10. Branched or star-branched polymers as claimed in claim 9 that are capped by one or more functional terminal groups, wherein the terminal groups are five-atom, six- π -electron heterocycles.

20 11. A lubricating oil composition comprising a major amount of a lubricating base oil and a minor amount of a substituted or unsubstituted reaction product of the process of any one of claims 1 to 7.

25 12. A fuel composition comprising a major amount of a base fuel and a minor amount of a substituted or unsubstituted reaction product of the process of any one of claims 1 to 7.

13. An additive concentrate comprising an inert carrier fluid and from 10 to 80 %w, based on the total concentrate, of a substituted or unsubstituted reaction product of the process of any one of claims 1 to 7.

30 14. Use of a substituted or unsubstituted reaction product of the process of any one of claims 1 to 7 as a dispersant, detergent or antioxidant additive or VI improver.

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15. Use of telechelic prepolymers as claimed in claim 8 or branched or star-branched polymers as claimed in claim 10 in the preparation of high molecular weight products, including networks and VI improvers.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/05472

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F10/00 C08F4/00 C08F2/38 C08F8/00 C08C19/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C08C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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